GPO PRICE $ ____________

OTS PRICE(S) $ ____________

Hard copy (HC) 2.00

Microfiche (MF) .50

FACILITY FORM 602

N65-16253	
(ACCESSION NUMBER)	(THRU)
33	1
(PAGES)	(CODE)
CR 60531	23
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Report No. IITRI-C6018-12
(Quarterly Report)

INVESTIGATION OF LIGHT SCATTERING
IN HIGHLY REFLECTING PIGMENTED COATINGS

National Aeronautics and Space Administration
Office of Advanced Research and Technology
Washington 25, D.C.

UNPUBLISHED PRELIMINARY DATA

Report No. IITRI-C6013-12
(Quarterly Report)

INVESTIGATION OF LIGHT SCATTERING IN HIGHLY REFLECTING PIGMENTED COATINGS

August 1 to November 1, 1964

Contract No. NASr-65(07)
IITRI Project C6018

Prepared by

G. A. Zerlaut, B. H. Kaye and V. Raziunas

Submitted by

IIT RESEARCH INSTITUTE
Technology Center
Chicago 16, Illinois

to

National Aeronautics and Space Administration
Office of Advanced Research and Technology
Washington 25, D. C.

Copy No. 21

December 21, 1964

FOREWORD

This is Report No. IITRI-C6018-12 (Quarterly Report) of Project C6018, Contract No. NASr-65(07), entitled "Investigation of Light Scattering in Highly Reflecting Pigmented Coatings." This report covers the period from August 1, 1964 to November 1, 1964. Previous Quarterly Reports were issued on October 11, 1963 (IITRI-C6018-3), January 29, 1964 (IITRI-C6018-6), May 5, 1964 (IITRI-C6018-8) and September 5, 1964 (IITRI-C6018-11).

Major contributors to the program include Gene A. Zerlaut (Project Leader), Dr. S. Katz and Dr. B. Kaye (theoretical analyses), and V. Raziunas (experimental investigator.)

Data are recorded in Logbooks C14085 and C13906.

Respectfully submitted,
IIT RESEARCH INSTITUTE

Gene A. Zerlaut
Group Leader
Polymer Research Section

APPROVED BY:

Theodore H. Meltzer
Manager
Polymer Research Section

ABSTRACT

INVESTIGATION OF LIGHT SCATTERING IN HIGHLY REFLECTING PIGMENTED COATINGS

16253

This report contains (1) a detailed discussion of the random-walk technique (for a collapsed cloud) which will be used in an attempt to elucidate the multiple scattering mechanisms in concentrated, polydisperse paint films, and (2) results of continued experiments to determine the optical properties of carefully prepared silver bromide arrays. The random-walk model proposed consists of an idealized series of energy/boundary encounters wherein the paint film is treated in a manner analogous to a series of diffraction screens consisting of random apertures. Integrated reflectance data of silver bromide arrays indicate that in back-scatter as in total scatter the particles tend to act as independent scatterers for energy penetration to a depth of from 2 to 4 layers of pigment.

Author

TABLE OF CONTENTS

List of Figures

INVESTIGATION OF LIGHT SCATTERING PARAMETERS ASSOCIATED WITH HIGHLY REFLECTING PIGMENTED COATINGS

I. INTRODUCTION

The principal objective of this program is the application of light-scattering theory to particle arrays in an attempt to explain the scattering behavior of polydisperse pigmented coatings, especially highly reflecting pigmented coatings. In this respect, the program is aimed at a definition of the light-scattering parameters that are necessary for the maximum reflection of solar radiation. The definition and explanation of these factors should facilitate the eventual development of more highly efficient solar reflectors and, perhaps more important, should serve to extend our ability to apply light-scattering theory to the solution of other complex problems involving a multiplicity of particles and size distributions.

Existing theory deals with single particles and with simple arrays of uniform size and spacing. The complexity of the mathematics dealing with light scattering has precluded the development of precise theoretical models which explain the considerably more complicated cases of concentrated three-dimensional arrays, expecially for systems with a multiplicity of sizes. Therefore, some of the questions -- which are in reality quite practical -- that this program hopes to answer are: What is the optimum particle-size distribution and particle concentration required for maximum reflection of the solar (as well as other sources) energy distribution? How closely must the idealized size and spacing be followed to achieve the desired results?

Previous quarterly reports have discussed (1) the applicable classical light-scattering theory, (2) the results of experiments concerning the optical properties of carefully prepared silver bromide suspensions and gelatin arrays, and (3) the initial conception of a random-walk technique with which to treat the problem of multiple scattering. Classical light scattering theory as it pertains to pigmented systems was discussed in IITRI Reports IITRI-C6018-3 (fully transparent spherical particles), IITRI-C6018-6 (partially absorbing and total reflecting, high index particles), and IITRI-C6018-11 (total reflecting spheres). The experimental program has concentrated on the establishment of the optical properties of carefully prepared suspensions (in water and in gelatin films) of silver bromide particles. These include studies of relatively monosized particles as well as of suspensions of (bimodal) mixtures of two narrow size distributions. More recent theoretical analyses have involved the generation of Monte Carlo, random-walk models which are being adapted to the problem of defining multiple interaction (i.e., multiple scattering).

This report contains a more detailed discussion of the random-walk techniques and establishes the rationale for this approach. The results of continued experimental investigations are also presented.

II. RANDOM-WALK TECHNIQUE FOR STUDYING MULTIPLE SCATTERING

In an earlier communication it was suggested that a random-walk summation of sequential energy encounters between scattered radiation and scattering particles can be used to calculate the effects of multiple scattering when radiation traverses a cloud of particles. When preliminary calculations were made of the average distances between particle centers to be expected in normal paint films of about 40% by volume solid concentration, it was found that there was a high probability that many of the surfaces of the particles would be in contact. This physically resembles the situation that occurs when the cloud considered in the first model collapses to a contiguous whole. The two main features of the collapsed cloud are the loss of identity by individual particles that are in intimate contact and the high density of scatters per unit volume.

In view of these special features of the closely packed pigment particle system, it was decided that a random walk consisting of a series of discrete particle/energy encounters may not be wholly appropriate, and a second random-walk model was developed for this type of system. In defense of the model given in this report, it should be noted that Van de Hulst has recently criticized current attempts to solve multiple scattering problems. He states that "too much emphasis has been placed upon redoing with better accuracy and more refined mathematical methods the problems for which rough answers are already available." He also points to the encouraging fact that "usually, the intuitively chosen solution turns out to be the correct one." By implication he exhorts the scientist to seek intuitive solutions to some of the more complex interaction problems. The model given here is an attempt to arrive at an intuitive solution to the light-scattering properties of a collapsed cloud of individual scattering particles.

Consider first the two-dimensional representation of the penetration of radiation through a section through a paint film shown in Figure 1. For this initial model it is assumed that all interstitial spaces are completely filled with paint vehicle.

It is pertinent to note that the arrows do not depict rays but only the directional flow of energy. The use of arrows to depict energy directions and to symbolize encounters of energy with boundaries between media of different refractive indices is consistent with the procedure followed in advanced texts concerned with wave optics theories. If it is preferred, the same type of reasoning based upon the use of Huygen's secondary wavelets in the diagrams would lead to the same result. At encounter 1 some of the energy is reflected, and some is transmitted. The reflected portion proceeds directly to encounter 2. The energy transmitted into the second medium at encounter 1 will proceed to the encounter 3. Again, at encounters 2 and 3 there will be partial reflection and transmission. Further sequence of events are suggested by the continuing lines drawn in Figure 1. Symbolically, the encounters of Figure 1 can be represented as shown in Figure 2. At encounter 1 the

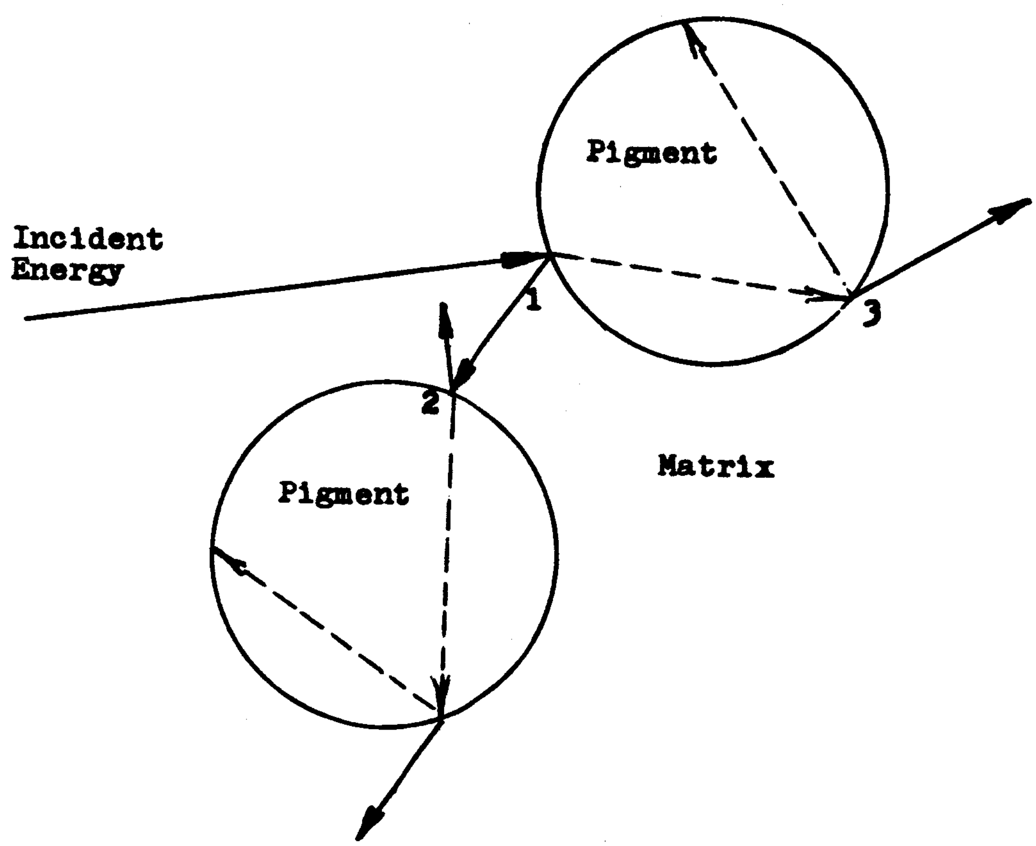

Figure 1

TWO DIMENSIONAL REPRESENTATION OF ENERGY ENCOUNTERS IN A PAINT MATRIX energy is separated into two parts, a reflected portion denoted by R and a transmitted portion, T. Each of these has associated with it a set of characterizing parameters: α, the directional function, Θ, the phase change with respect to the initial beam, S, a function of the absorption factor of the medium through which the energy is travelling and the optical path length P between encounters, β, the fraction of energy reflected or transmitted.

Now consider the energy incident on the surface to consist of random bursts of wavetrains. As each wavetrain tries to penetrate the matrix, the orientation of the boundaries will be completely at random. Therefore, all orientations are equally probable with respect to the incident direction. If a sufficiently large number of events are considered, it would seem reasonable to assume that half of the encounters reflect the energy forward and half backward. The reflection factor for determining the energy partition will have some average value taken over all individual values for all possible orientations. Let us assume that its value is α. Throughout the paint matrix the optical path length between energy-boundary encounters will vary between zero and an upper limit imposed by the characteristics of the paint matrix.

However, if enough events are considered, it would seem reasonable to assume that there is an average path length between encounters, which we will call d. Again, the number of events experienced in a sequential path will vary for a given sequence, but for a given paint film there will be some average

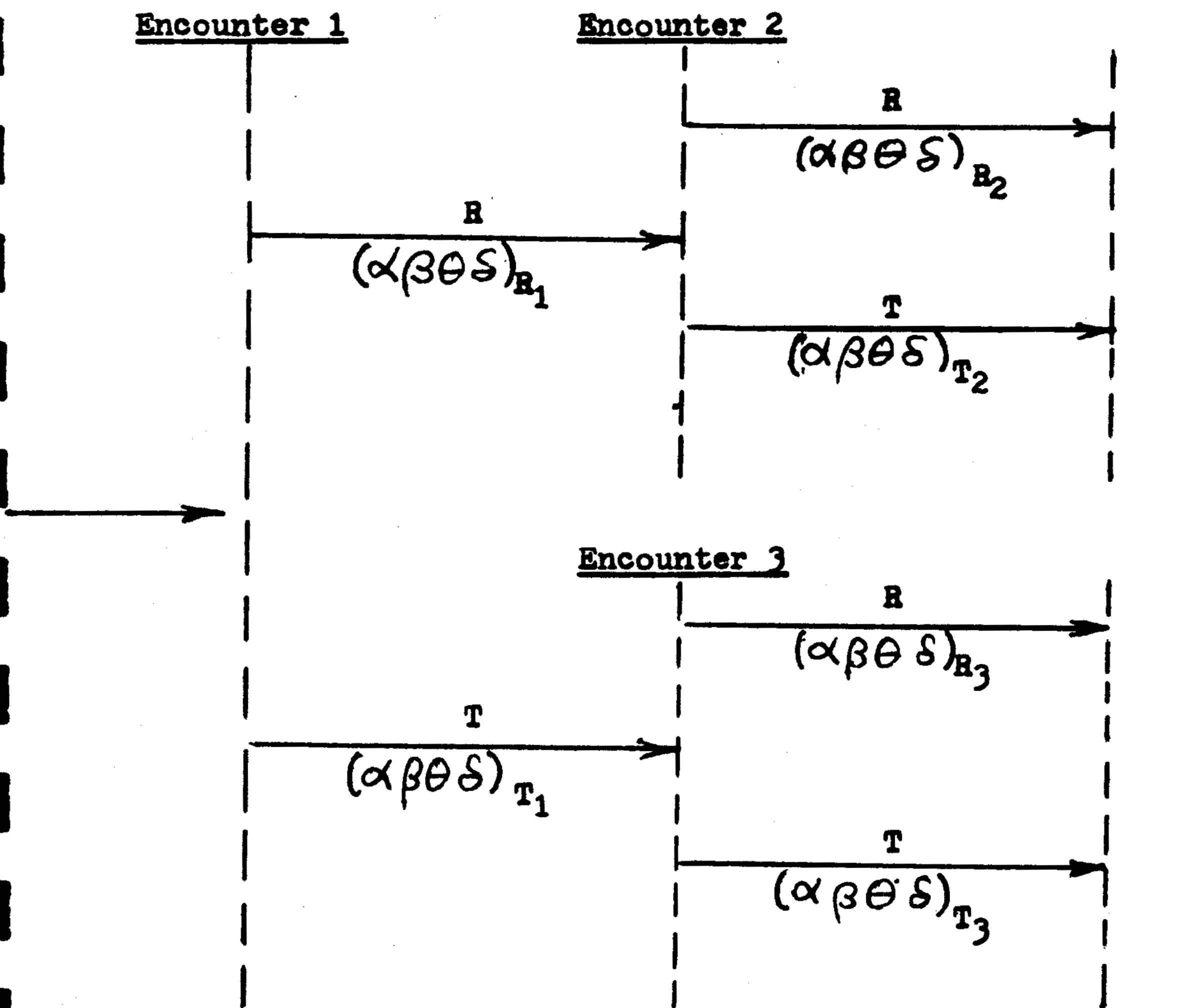

Figure 2

SYMBOLIC REPRESENTATION OF ENERGY/BOUNDARY ENCOUNTER

characteristic number of events that can be used when averaging the penetration of energy for many sets of events. If we consider the effects of many incident wavetrains of the same frequency travelling through the paint matrix, then the phase relationship between the many waves passing through a point chosen within the matrix will be distributed at random, i.e., all phase angles between 0 and 2π will be equally possible.

Consider first the simple case where all amplitudes of a wave be a and let there be n waves passing through a point in space. If these motions were all in the same phase, the resultant would be na and the intensity n^2a^2, or n^2 times that of one wave. In the case we are considering, however, the phases are distributed purely at random. If the graphical method of compounding amplitudes were used, we would now obtain a picture like Figure 3. The phases α_1, α_2 , ... take perfectly arbitrary values between 0 and 2π.

The intensity due to the superposition of such waves will now be determined by the square of the resultant A. To find A^2, we must square the sum of the projections of all vectors a on the x axis and add the square of the corresponding sum for the y axis. The sum of the x projections is

$$a(\cos\alpha_1 + \cos\alpha_2 + \cos\alpha_3 + \cdots + \cos\alpha_n) .$$

When the quantity in parentheses is squared, we obtain terms of the form $\cos^2\alpha_1$ and others of the form $2\cos\alpha_1\cos\alpha_2$. When n is large, the latter terms might be expected to cancel out, because they take both positive and negative values. In any one arrangement of the vectors this is far from true, however; in fact, the sum of these cross-product terms actually increases approximately in proportion to their number. Thus, we do not obtain a definite result with one given array of randomly distributed waves.

In computing the intensity in any physical problem, we are always presented with a large number of such arrays, and we wish to find their average effect. In this case, it is safe to conclude that the cross-product terms will average to zero, and we have only the $\cos^2 \alpha$ terms to consider. Similarly, for the y projections of the vectors $\sin^2\alpha$ terms are obtained, and their terms such as $2 \sin \alpha_1 \sin \alpha_2$ cancel. Therefore,

$$I \sim A^2 = \alpha^2(\cos^2 \alpha_1 + \cos^2\alpha_2 + \cos^2\alpha_3 \cdots + \cos^2\alpha_n) + a^2(\sin^2\alpha_1 + \sin^2\alpha_2 + \sin \alpha_3 + \sin^2\alpha_n)$$

Since $\sin^2\alpha_k + \cos^2\alpha_k = 1$, we find at once that

$$I \sim \alpha^2 \cdot n$$

Thus, the average intensity resulting from the superposition of n waves with random phases is just n times that due to a single wave.

The argument outlined above, which is taken from Fundamentals of Physical Optics by Jenkins and White, can readily be extended to the case of n waves when a is varying. However, now the average intensity would also be a function of the distribution of amplitudes. Therefore, for the purpose of judging the inten-

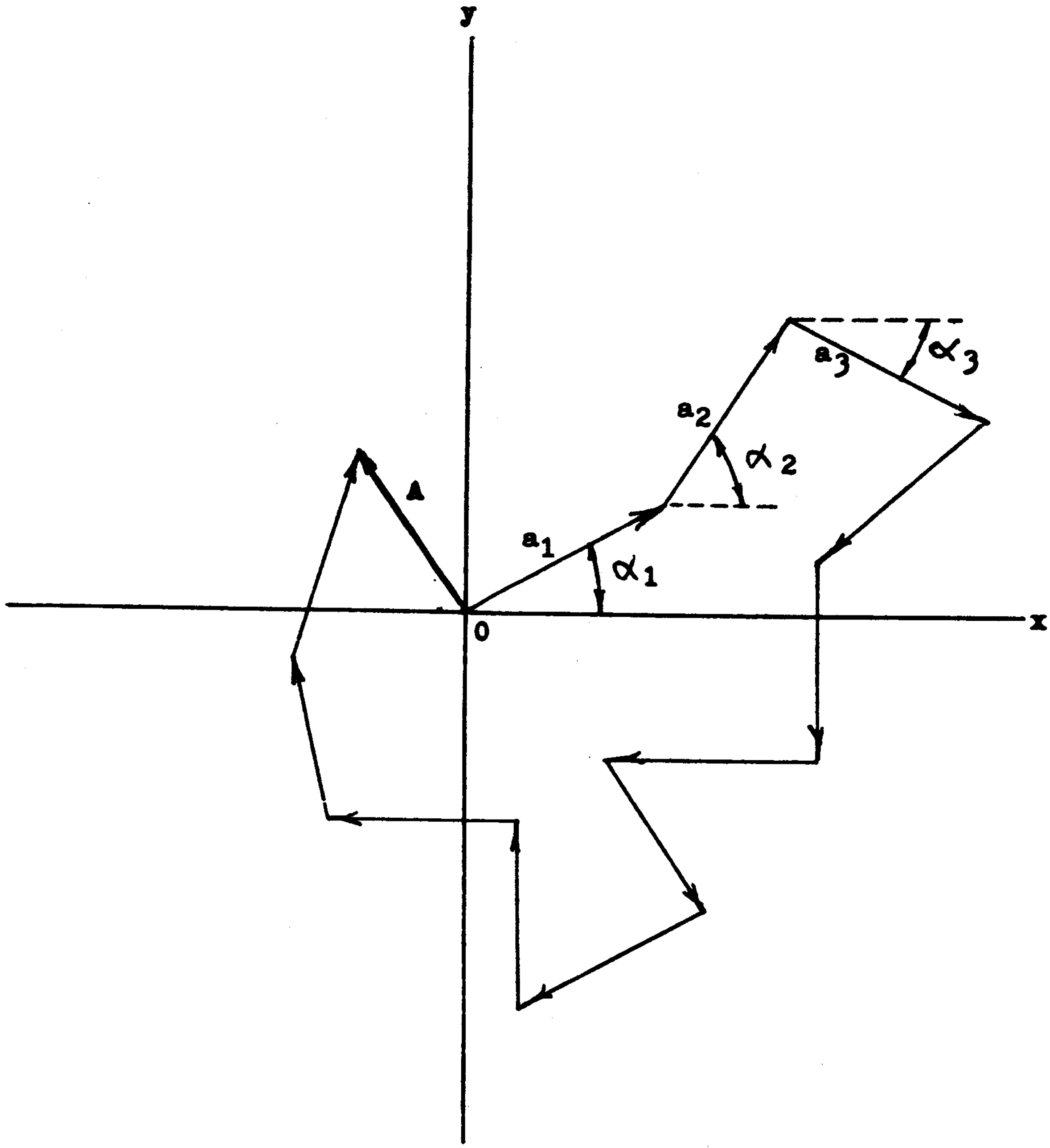

Figure 3

ILLUSTRATING THE RESULTANT OF 12 AMPLITUDE VECTORS DRAWN WITH THE PHASES AT RANDOM sities of the individual averaged energy flows.

By using these concepts of statistical averaging of many events, the flow of energy can be depicted as shown in Figure 4. We consider the flow of energy into unit area of paint film. On the average, the amount of pigment encountered in a unit plane is the same as the fractional volume concentration of pigment (H. Rumpf, Agglomeration, ed., Knepper, 1961, p. 379). If we denote the fractional volume of solids by E, the amount of incident energy, I, reflected is $I\alpha E$. The amount $I(1-\alpha)E$ is transmitted through the pigment while $I(1-E)$ is transmitted through the vehicle. For simplicity at this stage, it is assumed absorption is neglible, although it is possible to extend the model to allow for absorption.

In Figure 4 the results of three successive encounters are shown. Pictorial representation of a high number of encounters becomes cumbersome, but the number of events shown is sufficient to illustrate the principle. A further development of the model would be to allow for random fluctuation in E, which occurs when sections are taken (through a paint film). The model shown in Figure 4 is obviously related to the Kubelka-Munk model with the reflectance and scattering coefficient of the Kubelka-Munk derivation given physical significance in relation to the property of the reflectance of the particles, the total surface of the particles (in the number of interfaces considered per unit area), and in the packing properties of the paint pigment in the film considered.

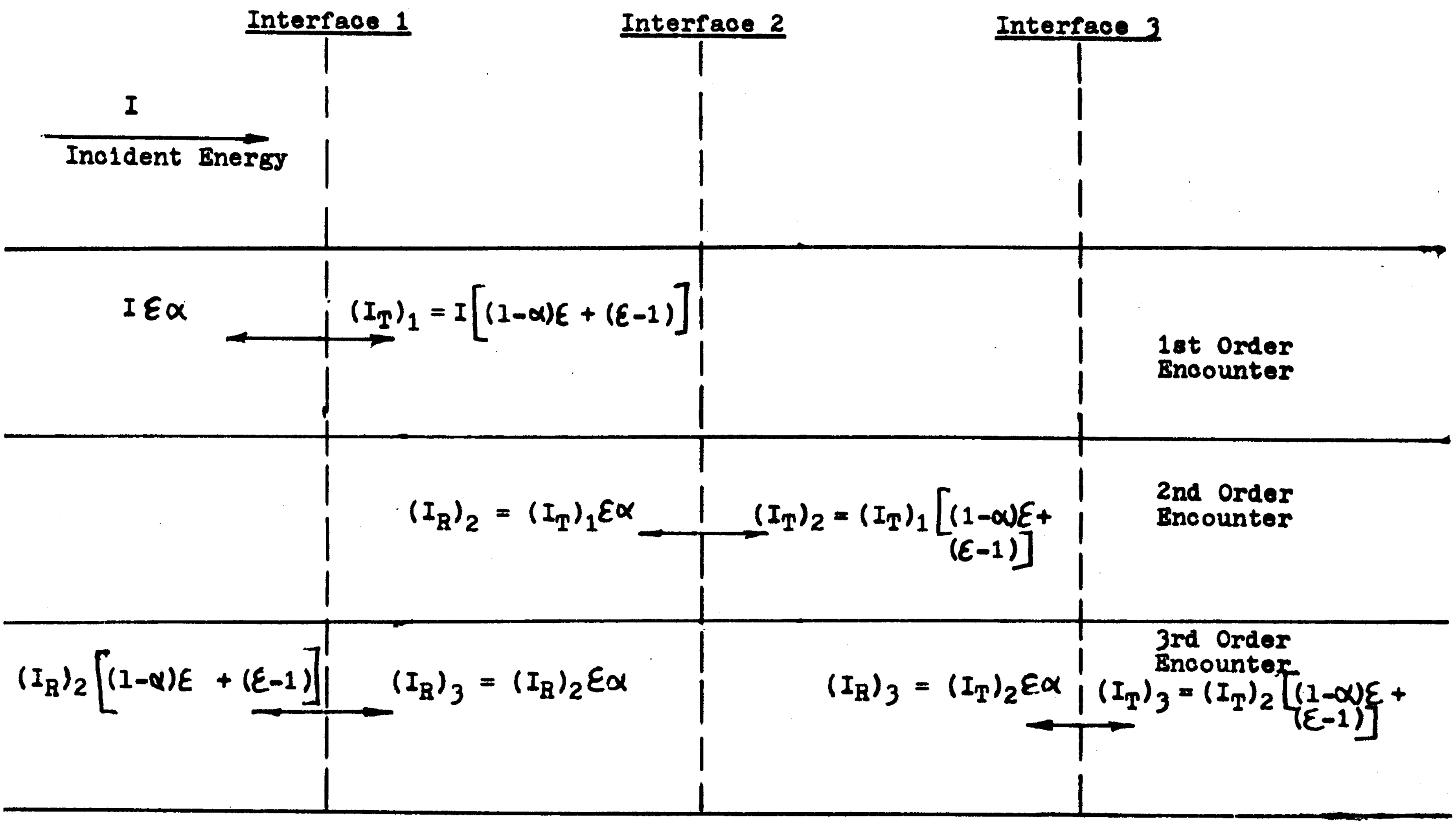

Figure 4

IDEALIZED SERIES OF ENERGY/BOUNDARY ENCOUNTERS

It should be noted that a possible physical explanation of the proposed model is that the paint film is being treated as a series of diffraction screens consisting of random apertures -- the radiation being homogenized between successive encounters.

III. EXPERIMENTAL STUDIES

A. Introduction

The spectral transmittance properties of exceedingly thin (approximating a monolayer), concentrated films of silver bromide in gelatin suspensions were given in our last report.[1] Sets of three films were compared, in each case; two obtained from monodisperse suspensions and one of their bimodal mixture. It was shown that the experimentally obtained optical density of the mixture was closely approximated by the constructed sum of the optical densities of single particle suspensions at half the concentration. Since the films were exceedingly thin (0.4 to 1.0 μ) their thicknesses were assumed to be approximately equal.

During this research period several sets of thicker films were prepared containing monodisperse and bimodal mixtures. Such films gave a more realistic approximation of a real, pigmented paint. Also the films were made sufficiently thick so that the backscatter (hemispherical reflectance measurements) could be obtained.

---

[1]Report No. IITRI-C6018-11 (Quarterly Report), August 1964.

The thicknesses of the above films were measured interferometrically[2], and the assumption of equal thickness was eliminated by the introduction of the measured values in the extinction equations (see Equations 3 and 4).[3]

The integrated reflectance (nondisperse, diffuse and monochromatic, parallel illumination) measurements have been completed and the data have been partially reduced. Some preliminary comparisons of the reflectance data is given in this report, and the reduction should be completed during the next research period.

Our intermediate objective is to obtain experimentally a complete balance of radiant energy after interaction with the semitransparent pigmented films, e.g., parallel and diffuse transmittance intensities and integrated reflectance intensities with and without the specular component.

B. Thickness and Concentration of Semitransparent Films

The thicknesses were measured interferometrically using a Zeiss model 2300 interference microscope as noted previously.[2] The concentrations of the monodisperse scatterers were calculated from the optical density at wavelengths corresponding to the midpoint between the first scattering maximum and the minimum,[4] and using the extinction equation

$$D = K\pi r^2 \eta \cdot \ell$$

where D is the optical density (to the base of the natural log),

[2]Report No. IITRI-C6018-8 (Quarterly Report), May 5, 1964.

[3]Report No. IITRI-C6018-11 (Quarterly Report), September 5,1964,p.12.

K is the total Mie scattering coefficient, r is the particle radius, n is the particle concentration (number/unit volume, and ℓ is the optical path length or the thickness of the films. The concentration may be expressed also as the particle separation in terms of the particle diameter for monodisperse suspensions: no π particle separation (diameters = $\frac{1}{n^{1/3} \cdot 2r}$; a cubic lattice of packing is inherently assumed in the above and separation is expressed in the number of diameters between the particle centers.

For the bimodal mixtures (50/50% by weight) the concentrations were assumed to be half of the concentrations of the components of the mixture. There seems to be no convenient method of experimentally measuring concentrations in dry films of bimodal mixtures. The thickness and concentration measurements are summarized in Table 1.

C. The Transmittance Properties of Simulated Bimodal Coatings

Sets of three films as noted in our previous report[5] were compared; a sum of the optical densities of two monodisperse films at 50% of original concentration was compared with the optical density of the bimodal mixture. The spectral curves of monodisperse suspensions were normalized to the thickness of the bimodal mixture using the thickness measurements given in Table 1. The data are summarized in Figures 5 to 7, indicating that the two size particles tend to act as independent scatterers in

[4] Report No. IITRI-C6018-8 (Quarterly Report), May 5, 1964,p.24.

[5] Report No. IITRI-C6018-11 (Quarterly Report), September 5, 1964 p. 11.

Table 1

THICKNESS AND CONCENTRATION OF SILVER BROMIDE FILMS

Batch No.	Radius, μ (r)	Thickness, μ (ℓ)	Concentration, (n)	Separation (in Diameters)
25; A,	0.39	1.98	1.5	1.07
B,	0.39	1.54	1.75	1.04
26	0.32	1.68	2.63	1.14
30	0.20	1.67	9.7	1.18
39	0.15	1.24	-	-
40	0.07	1.94	-	-
Mixtures:				
25A + 26		1.88	-	-
25B + 30		1.76	-	-
39 + 40		1.5	-	-

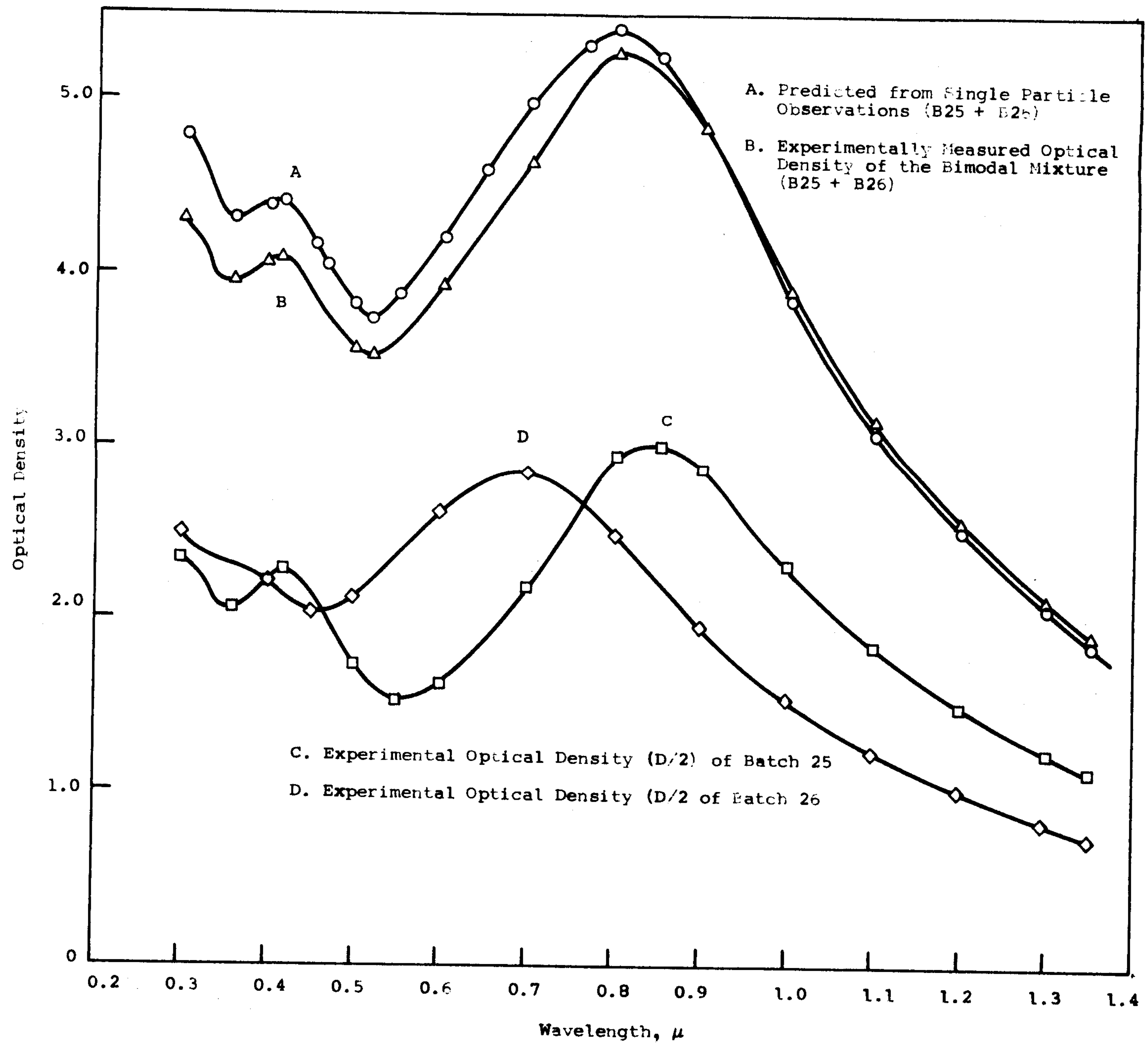

Figure 5

OPTICAL DENSITY OF SILVER BROMIDE SUSPENSIONS (BATCHES 25 AND 26)

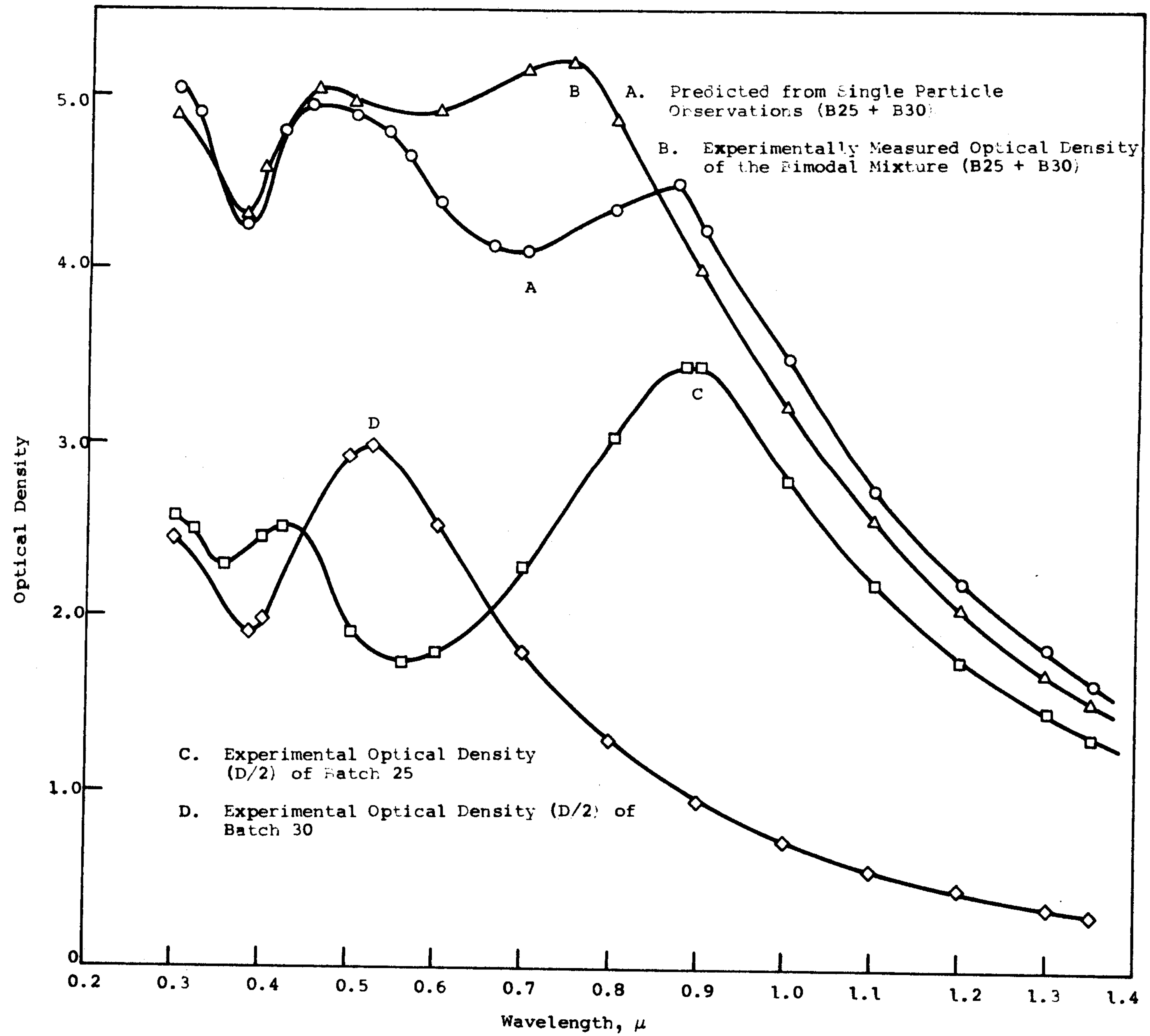

Figure 6

OPTICAL DENSITY OF SILVER BROMIDE SUSPENSIONS (BATCHES 25 AND 30)

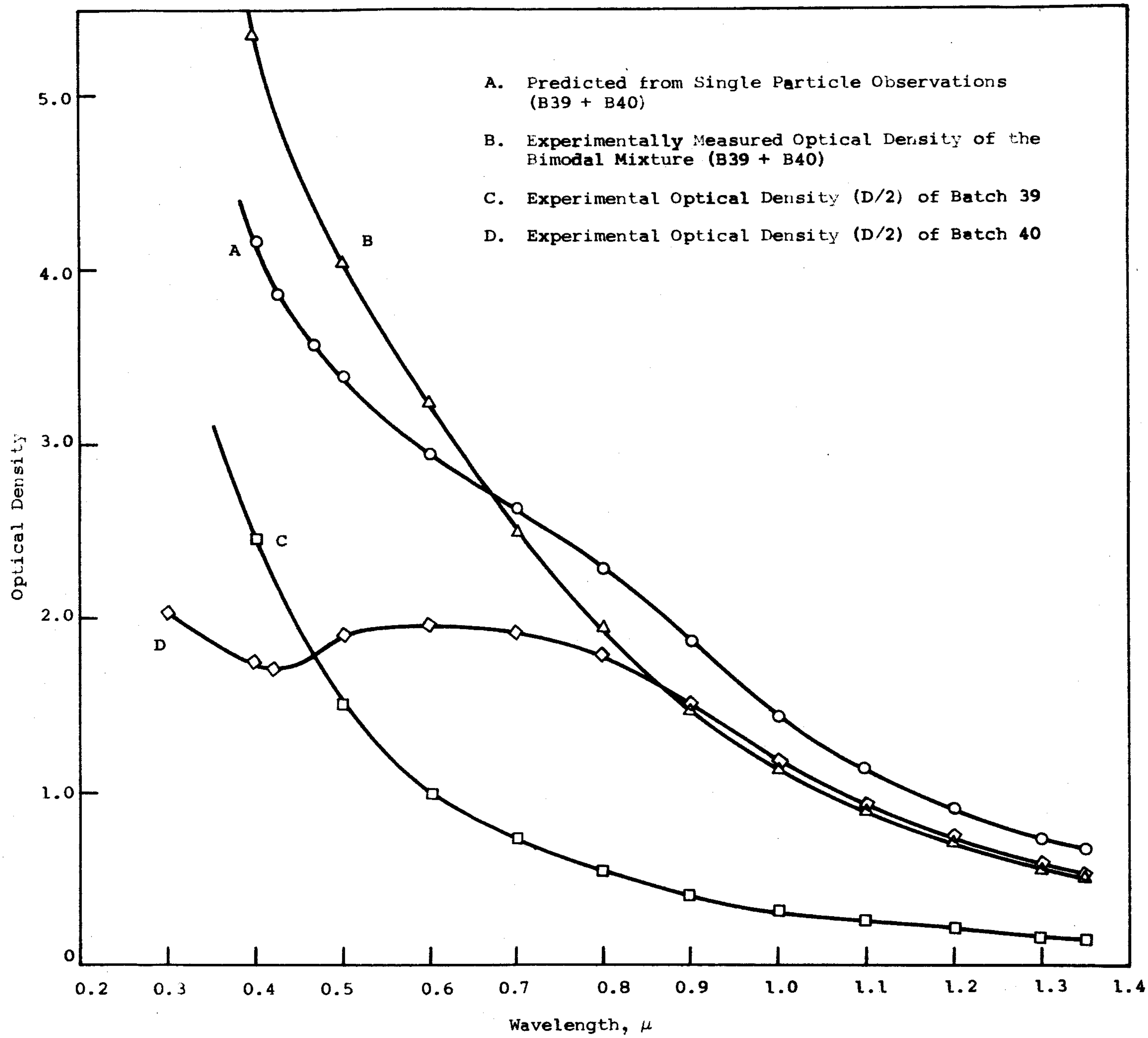

Figure 7

OPTICAL DENSITY OF SILVER BROMIDE SUSPENSIONS (BATCHES 39 AND 40)

concentrated films containing several layers of pigment.

It should be emphasized again that our greatest source of error in such a comparison is probably the measurement of thickness. Since the films are very thin, an error of ± 15% may be expected. The effects of thickness correction may be noted in Figure 8, which represents the most extreme case we have observed thus far.

D. The Hemispherical Reflectance of Simulated Bimodal Coatings

The total hemispherical reflectance of previously described semitransparent films were measured by using nondispersed, diffuse illumination and monochromatic, parallel illumination at normal incidence. The reduction of these data has not been completed at this point. It should be pointed out that an identical spot on each film (approximately 2 x 2 mm area) was used for all measurements (transmittance, reflectance, and thickness).

Some of the hemispherical reflectance data, in relative logarithmic intensity units, are given in Figures 9 to 11. The measurements were made with a magnesium carbonate block standard using monochromatic, parallel illumination. The data indicate that in backscatter as in total scattering the particles tend to act as independent scatters for energy penetration to a depth of 2 to 4 layers of pigment.

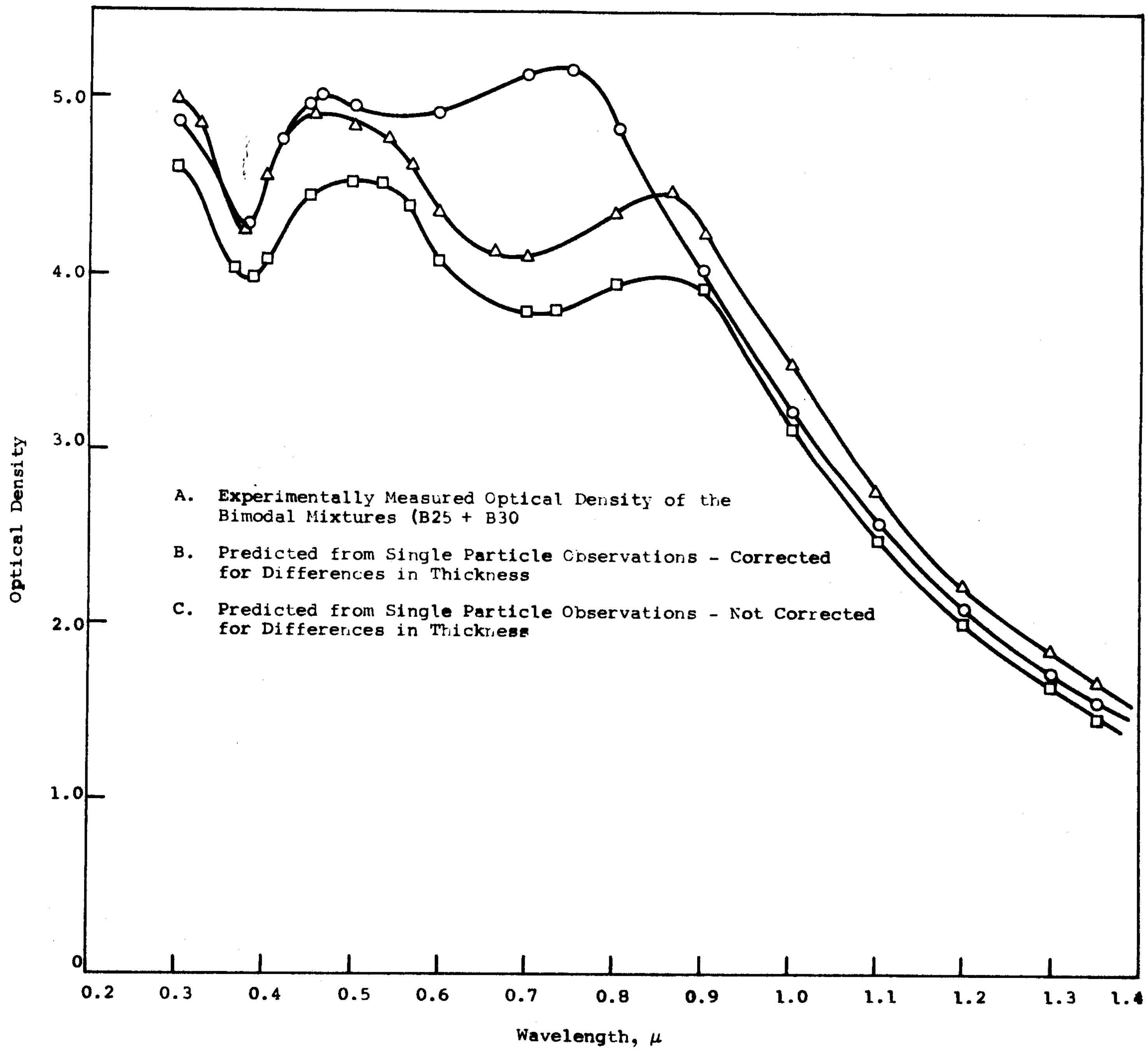

Figure 8

THE EFFECT OF THICKNESS CORRECTION

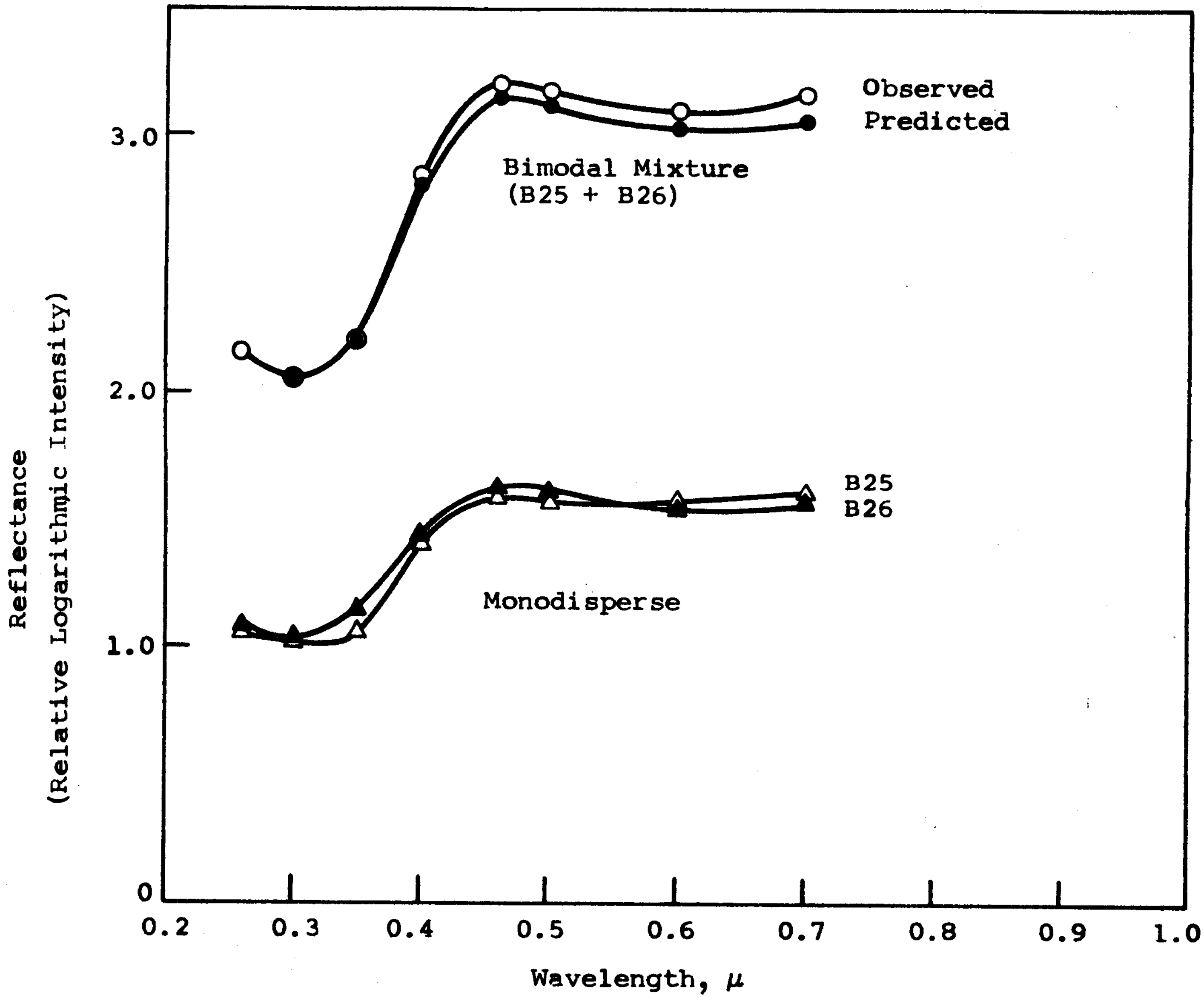

Figure 9

THE REFLECTIVITIES OF SILVER BROMIDE FILMS

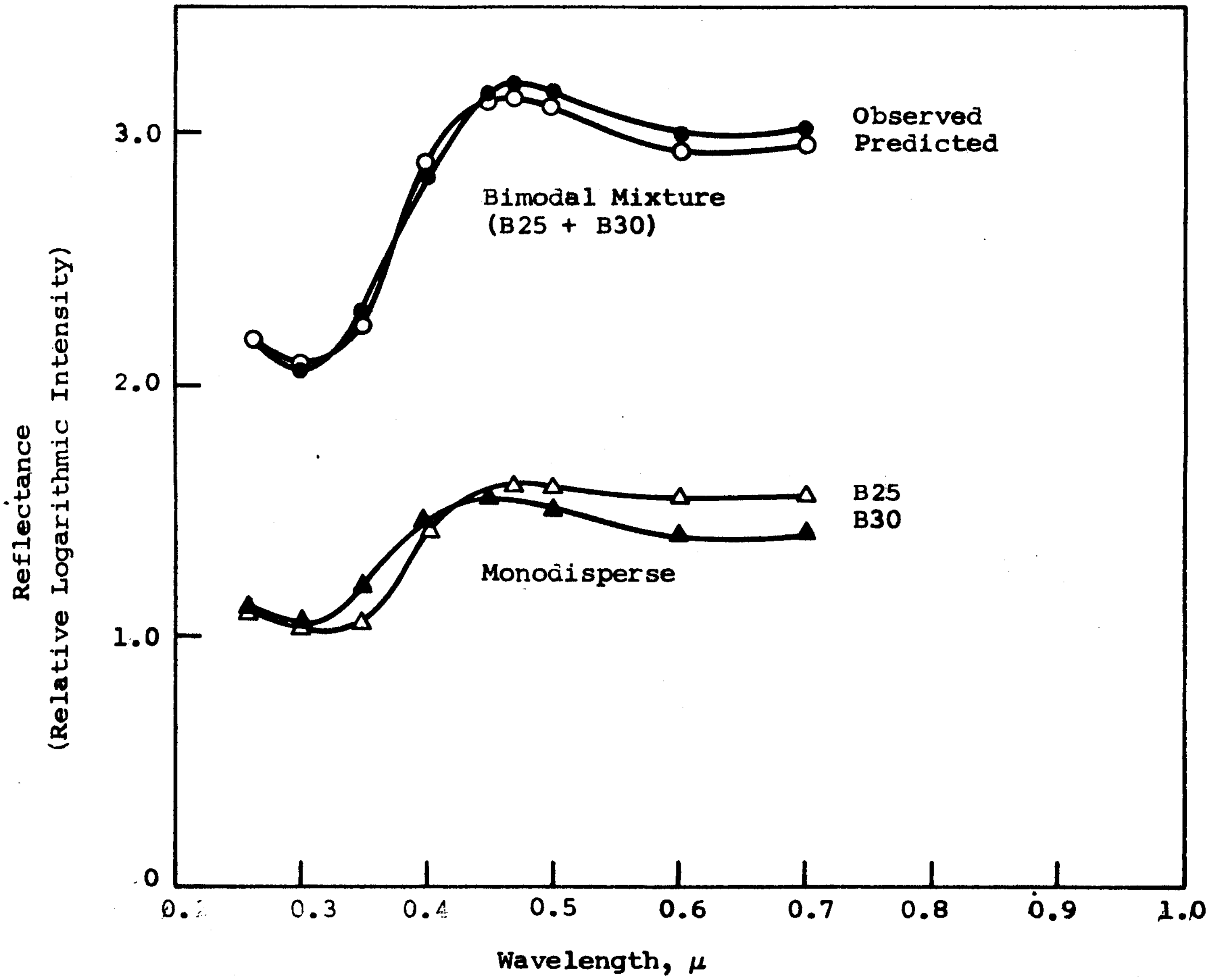

Figure 10

THE REFLECTIVITIES OF SILVER BROMIDE FILMS

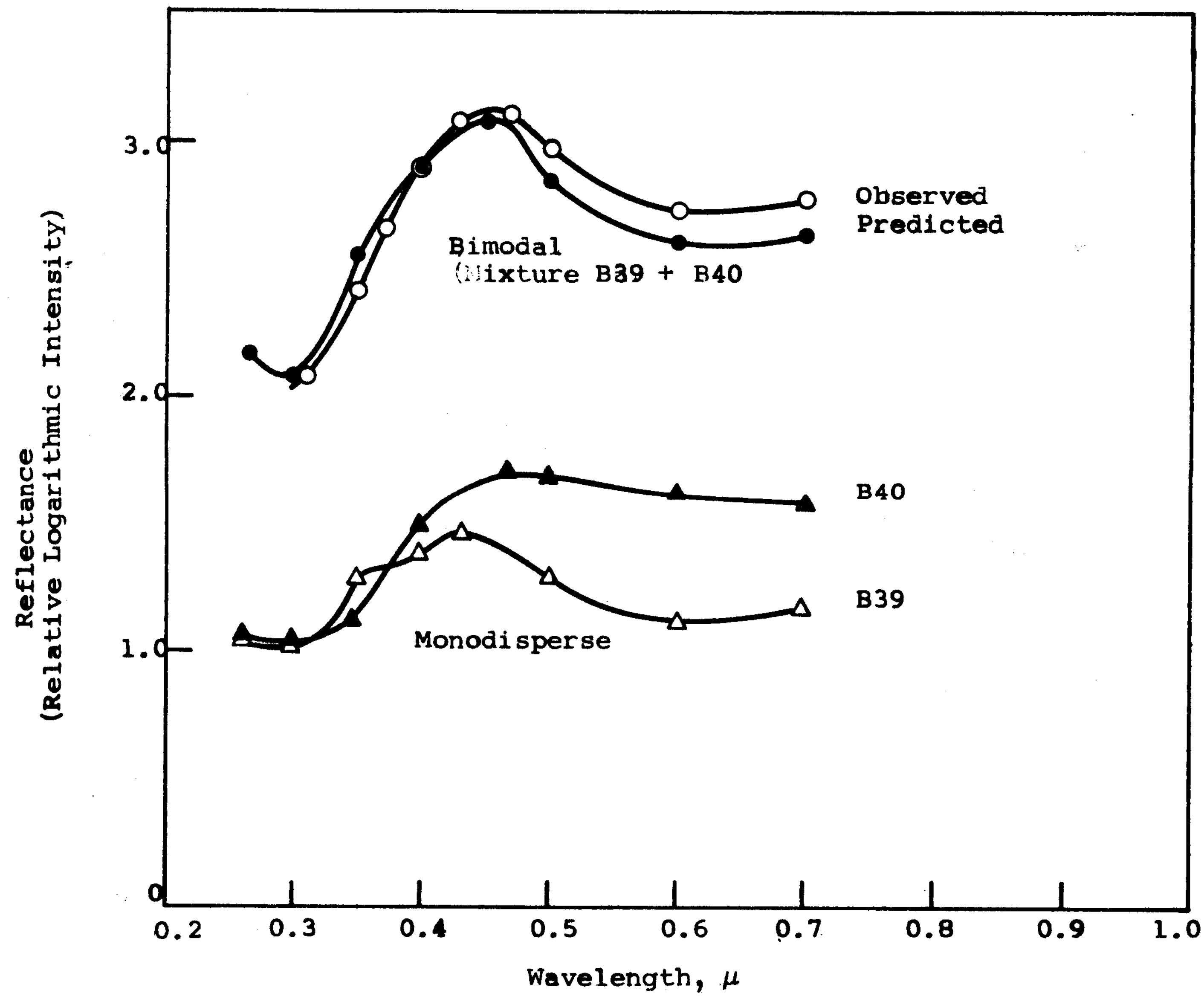

Figure 11

THE REFLECTIVITIES OF SILVER BROMIDE SUSPENSIONS

IV. DISCUSSION OF FUTURE WORK

A. Classical Light-Scattering Theory

The present study is being extended by the application of Mie theory to three-dimensional particle arrays. The initial emphasis is on monodisperse arrays of very high refractive index -- the so-called totally reflecting spherical particles. Either subsequently or concurrently the scatter of transparent particle arrays will be considered.

B. Random-Walk Technique for Studying Multiple Scattering

The original concept of random-walk sequence will be applied to a dilute cloud system. Trial calculations will be undertaken to determine the validity of the approach. The behavior of the mathematical model as the cloud concentration increases will be studied and the physical significance of the model predictions explored.

The second type of random-walk model for systems in which the individual scatterers have started to lose their separate identity will be further developed. Calculations will be performed to determine whether useful physical predictions can be made concerning the scattering properties of a dense paint.

C. Experimental Studies of Silver Bromide Arrays

The reflectance data will be reduced and related to the transmittance measurements during the next research period. Attempts will be made to normalize the data so that a detailed account of the distribution of the radiant energy may be obtained by comparing the total rate of energy loss (transmitted intensity) with the rate of backscattered energy (integrated reflectivity with various modes of illumination). Attempts will be made to relate all of the above measurements to the theoretical values predicted by the single particle scattering theory.

It is visualized that some of the optical measurements applicable to semitransparent films with rigidly defined physical parameters (such as particle size distribution, particle concentration, thickness, effective refractive index) may be extended to thick, completely opaque films of identical composition. Such a film would represent a true paint, therefore, by gradually increasing the thickness of semitransparent films, it may be feasible to elucidate radiative interactions occurring in real pigmented systems.

In our previous report [6], we stated a set of hypothetical requirements for an ideal highly reflecting coating based on

---

[6] Report No. IITRI-C6018-11, (Quarterly Report) September 5, 1964, pp. 27-30.

transmittance measurements. One of the requirements was that such a coating should consist of layers of particles of increasing size with respect to the incident beam. The radiant energy balance within such a model shall be further considered and elaborated in future reports. Attempts will be made to test experimentally the validity of such a model.

Distribution List:

Copy No.	Recipient
1-25 + re producible	National Aeronautics and Space Administration Office of Grants and Research Contracts Washington, D.C.
26	Mr. J. J. Gangler National Aeronautics and Space Administration Office of Advanced Research and Technology Washington 25, D.C.
27-30 + reproducible	Mr. D. W. Gates (M-RP-T) George C. Marshall Space Flight Center Huntsville, Alabama
31	Mr. Conrad Mook Code RV National Aeronautics and Space Administration Washington, D.C.
32	Mr. William F. Carroll Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, California
33	Mr. Sam Katzoff National Aeronautics and Space Administration Langley Research Center Langley Field, Virginia
34	Mr. Joseph C. Richmond National Bureau of Standards Washington, D.C.
35	Mr. James Diedrich, Mail Stop 7-1 Lewis Research Center Cleveland, Ohio
36	IIT Research Institute Division C Files
37	IIT Research Institute Editors, J. J. Brophy, J. I. Bregman, Main Files

Distribution List: (continued)

Copy No.	Recipient
38	IIT Research Institute K. W. Miller, Report Library
39	IIT Research Institute Y. Harada, Division B
40	IIT Research Institute E. H. Tomplins, Division C
41	IIT Research Institute G. A. Zerlaut, Division C
42	IIT Research Institute S. Katz, Division C
43	IIT Research Institute B. Kaye, Division C